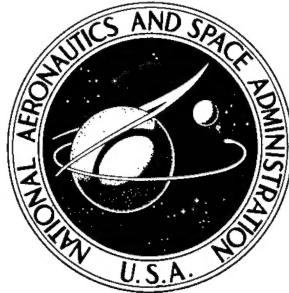


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# POLYIMIDES FROM SOME DIAMINOANTHRAQUINONES AND PYROMELLITIC DIANHYDRIDE

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# POLYIMIDES FROM SOME DIAMINOANTHRAQUINONES AND PYROMELLITIC DIANHYDRIDE

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## SUMMARY

Two new thermally stable polyimides were synthesized from pyromellitic dianhydride (PMDA) and two isomeric diaminoanthraquinones. The synthesis was accomplished through ester-blocked polyimide prepolymers by using methanol as the blocking reagent. The reaction of PMDA with methanol gave a diester-diacid, which was converted to the corresponding diester-diacid chloride with thionyl chloride. The reaction of equivalent amounts of the diester-diacid chloride and diaminoanthraquinone in N,N-dimethylacetamide solution gave the soluble ester-blocked polyimide prepolymer. The prepolymers were converted to the corresponding polyimides by thermal cyclization at 300° C.

Several properties of the ester-blocked prepolymers and polyimides were studied. The blocked prepolymer poly[2,6-anthraquinylene-2,5-bis(carbomethoxy)terephthalamide](V) (2,6-DAQ BPP) from PMDA and 2,6-diaminanthraquinone was more resistant to thermal imidization than the corresponding unblocked polyamic acid when heated for 2 hours at 200° C. The blocked prepolymer from PMDA and 1,5-diaminoanthraquinone showed no imidization under these conditions.

The weight-average molecular weight of 2,6-DAQ BPP was increased from 8500 to 16,800 by the technique of solid-state polymerization. The prepolymer 2,6-DAQ BPP was still completely soluble after solid-state polymerization.

The 2,6-DAQ BPP exhibited excellent solvolytic stability. Its solutions in both anhydrous and aqueous N,N-dimethylacetamide showed no viscosity decrease for 510 hours at 25° C.

The two polyimides showed excellent thermal stability, as measured by thermogravimetric analysis. The polyimide poly[1,5-anthraquinylene-pyromellitimide](X) (1,5-DAQ PI) from PMDA and 1,5-diaminoanthraquinone was stable up to 500° C in both air and nitrogen. The isomeric polyimide poly[2,6-anthraquinylene-pyromellitimide] (VI) (2,6-DAQ PI) from PMDA and 2,6-diaminoanthraquinone was stable up to 550° C under the same conditions. A powdered sample of 2,6-DAQ PI retained 88 percent of its original weight on isothermal aging in air at 316° C (600° F) for 1000 hours. The weight retention was 75 percent when aging was carried out at 343° C (650° F).

## INTRODUCTION

Many current aerospace programs have established the need for polymeric materials that retain their useful properties at elevated temperatures. One important application of such polymers is their use as matrix materials in fiber-resin composites. In recent years, a considerable number of thermally stable polymers has been synthesized. These polymers exhibit thermal stabilities (as determined by thermogravimetric analysis) in excess of 500° C. There is a continued effort to extend the upper temperature limits of polymers for use in fiber-resin composites. This can be accomplished by (1) synthesis of entirely new polymer systems or (2) chemical modification of existing polymers. Our recent work has been concentrated in a related area, namely the improvement of processibility of existing polyimide resins by chemical modification of the prepolymers (ref. 1). It was felt that incorporation of anthraquinone repeating units into polyimides would increase the solubility of the resin. At the same time, Marvel (ref. 2) has suggested that the presence of anthraquinone repeating units would improve the thermal stability of a polymer. He has prepared polybenzimidazoles, polyimidazopyrrolones, and polyquin-oxalines containing anthraquinone residues. These polymers exhibited excellent thermal stability (ref. 2). There is, however, no mention of polyimides containing anthraquinone units in the literature.

This report describes the synthesis of new polyimides from pyromellitic dianhydride and two isomeric diaminoanthraquinones. The polyimides were prepared through a chemically modified, or blocked, polyimide prepolymer. The modified prepolymer offers several advantages over the conventionally used polyamic acid prepolymer: (1) The solvolytic stability of the modified prepolymer is expected to be better; (2) the modified prepolymer can be isolated as a solid and its molecular weight increased by the technique of solid-state polymerization; (3) the modified prepolymer is expected to be more resistant to thermal imidization.

In this work, solid-state polymerization and solvolytic stability of the chemically modified prepolymer were studied. Thermal stability of the final polyimides was determined by thermogravimetric analysis in air and nitrogen, as well as by isothermogravimetric analysis in air.

## EXPERIMENTAL PROCEDURE

### Reagents

N,N-dimethylacetamide (DMAc). - Technical grade DMAc was distilled in dry equipment under nitrogen and stored over molecular sieve 5A.

Pyromellitic dianhydride (PMDA (I)). - Technical grade PMDA was sublimed at  $220^{\circ}$  to  $240^{\circ}$  C and  $10^{-2}$  torr.

Methanol and thionyl chloride. - These reagent grade chemicals were used as received.

2, 6-Diaminoanthraquinone (2, 6-DAQ(IV)) and 1, 5-diaminoanthraquinone (1, 5-DAQ(VIII)). - Technical grade material was crystallized by addition of water to a hot solution of the diamine in N, N-dimethylformamide.

## Compound Synthesis

2, 5-Dicarbomethoxyterephthalic acid (DMTA(II)). - PMDA powder (21.8 g,  $1.00 \times 10^{-1}$  mole) was added to dry methanol (200 ml). The mixture was stirred under reflux until PMDA had dissolved (45 min). The clear solution was concentrated to approximately 100 milliliters and allowed to stand at room temperature for 24 hours. The solid that had precipitated was filtered off and dried in air to give a crude yield of 16.4 grams of DMTA with a melting point of  $222^{\circ}$  C. Crystallization from methanol gave 10.2 grams (36 percent) of pure DMTA with a melting point of  $237^{\circ}$  C. The literature (ref. 3) gives a melting point of  $238^{\circ}$  C.

2, 5-Dicarbomethoxyterephthaloyl chloride (DMTC(III)). - DMTA (8.46 g,  $3.00 \times 10^{-2}$  mole) was added to 30 milliliters of thionyl chloride containing a few drops of DMAc. The reaction flask was fitted with a drying tube. The mixture was stirred under reflux for 1 hour. During this time, the DMTA had dissolved. The excess thionyl chloride was removed by distillation under reduced pressure. The solid residue was crystallized twice from benzene-hexane (1:1 by volume). The yield of pure DMTC was 6.30 grams (66 percent) with a melting point of  $136.5^{\circ}$  to  $137.5^{\circ}$  C. The literature (ref. 3) gives a melting point of  $136.5^{\circ}$  to  $138^{\circ}$  C.

Poly[2, 6-anthraquinylene-2, 5-bis(carbomethoxy)terephthalamide] (2, 6-DAQ BPP(V)). - A suspension of 2, 6-DAQ (2.38 g,  $1.00 \times 10^{-2}$  mole) in dry DMAc (25 ml) was placed in a flask fitted with a nitrogen inlet, a magnetic stirrer, a drying tube, and an addition funnel. A solution of DMTC (3.19 g,  $1.00 \times 10^{-2}$  mole) in dry DMAc (30 ml) was added by drops through the addition funnel over a period of 15 minutes. A surge of temperature to  $50^{\circ}$  C occurred, but the temperature gradually returned to  $25^{\circ}$  C. The reaction mixture was stirred at room temperature for 4 hours under a stream of nitrogen. The solid 2, 6-DAQ dissolved gradually during the first 30 minutes. The solution was filtered, and the product was precipitated by adding acetone (400 ml) to the rapidly stirred solution. The orange precipitate was filtered and washed thoroughly with acetone. The product was dried at  $70^{\circ}$  C for 30 minutes to give a yield of 2.98 grams (62 percent) of 2, 6-DAQ BPP.

Poly[2, 6-anthraquinonylenepyromellitic acid](2, 6-DAQ PAA(VII)). - The polyamic acid was prepared according to the method of Sroog et al. (ref. 4). A suspension of 2, 6-DAQ (2.38 g,  $1.00 \times 10^{-2}$  mole) in dry DMAc (40 ml) was placed in a flask fitted with a nitrogen inlet, a magnetic stirrer, and a drying tube. Powdered PMDA (2.18 g,  $1.00 \times 10^{-2}$  mole) was added to the vigorously stirred suspension through a powder funnel. Residual traces of PMDA were washed in with 5 milliliters of dry DMAc. The reaction mixture was stirred at room temperature under a slow nitrogen stream for 2 hours. The solids dissolved gradually during the first 30 minutes. The solution was filtered, and the product precipitated by adding acetone (100 ml) to the rapidly stirred solution. The orange precipitate was filtered, washed with acetone, and dried at  $70^{\circ}$  C for 30 minutes. The yield of 2, 6-DAQ PAA was 2.06 grams (45 percent).

Poly[2, 6-anthraquinonylenepyromellitimide](2, 6-DAQ PI(VI)). - The polyimide was prepared by heating either 2, 6-DAQ PAA or 2, 6-DAQ BPP to  $300^{\circ}$  C at a rate of  $10^{\circ}$  C per minute and maintaining the temperature at  $300^{\circ}$  C for 1 hour.

Analysis calculated for  $(C_{24}H_8N_2O_6)_n$ : C, 68.58 percent; H, 1.92 percent; N, 6.67 percent. Found: C, 68.27 percent; H, 2.22 percent; N, 6.42 percent.

Poly[1, 5-anthraquinylene-2, 5-bis(carbomethoxy)terephthalamide](1, 5-DAQ BPP(IX)). - A suspension of 1, 5-DAQ (476 mg,  $2.00 \times 10^{-3}$  mole) in dry DMAc (8 ml) was placed in a flask fitted with a nitrogen inlet, a magnetic stirrer, a drying tube, and an addition funnel. A solution of DMTC (638 mg,  $2.00 \times 10^{-3}$  mole) in dry DMAc (14 ml) was added by drops through the addition funnel over a period of 10 minutes. The reaction mixture was stirred at room temperature under a stream of nitrogen for 20 hours. Addition of acetone (100 ml) to the reaction mixture precipitated an orange solid. The solid was collected by filtration, washed with acetone, and dried in air to give a yield of 98 milligrams (10 percent) of 1, 5-DAQ BPP. The weight-average molecular weight  $\bar{M}_w$  of the product was 8600. The filtrate was concentrated to approximately 20 milliliters by evaporation, and water (100 ml) was added. A total yield of 360 milligrams was precipitated. This fraction consisted of low-molecular-weight oligomer ( $\bar{M}_w$  of approx 1000).

Poly[1, 5-anthraquinonylenepyromellitimide](1, 5-DAQ PI(X)). - The polyimide was prepared by heating 1, 5-DAQ BPP to  $300^{\circ}$  C at a rate of  $10^{\circ}$  C per minute and maintaining the temperature at  $300^{\circ}$  C for 2 hours. An elemental analysis of 1, 5-DAQ PI was not performed, since the entire polyimide sample was used up in other studies of its properties.

### Molecular Weight Determination

The weight-average molecular weights  $\bar{M}_w$  of the polyimide prepolymers were calculated from the Mark-Houwink equation determined by Wallach (ref. 5):

$$\eta_{inh} = 2.47 \times 10^{-4} \bar{M}_w^{0.77}$$

The inherent viscosity  $\eta_{inh}$  measurements were carried out at 25° C and a concentration of 0.5 gram per deciliter with a Ubbelohde viscometer. The solvent was anhydrous DMAc, 0.1 N in lithium bromide.

### Solid-State Polymerization

The polymer was ground into a fine powder (60 to 80 mesh). The sample was packed into a glass column with an inside diameter of 7.5 millimeters. The packed column was installed in a gas chromatograph oven. After the flow of the helium carrier gas was adjusted to 300 milliliters per minute, the oven was heated and maintained at the desired reaction temperature for a specified time. The product was allowed to cool under the flow of helium. It was then stored in a gas-tight container to avoid moisture absorption.

### Solvolytic Stability Studies

The polymer samples were dissolved in (1) anhydrous DMAc and (2) DMAc containing 1 percent water by volume. The total concentration of the polymer was 0.5 gram per deciliter. The solvolytic stability was measured by observing the change in  $\eta_{inh}$  of the polymer solutions as a function of time. The polymer solutions were stored at room temperature for the duration of the experiment, and  $\eta_{inh}$  was measured at 25° C.

### Thermal Stability Studies

Thermogravimetric analyses were carried out in dynamic air and nitrogen atmospheres at a constant temperature rise of 10° C per minute. Isothermogravimetric analyses were performed in air for a period of 1000 hours at the specified temperatures. Powdered polyimide samples with a particle size of 60 to 80 mesh were used in all experiments.

## RESULTS AND DISCUSSION

### Synthesis of Polymers

Aromatic polyimides are commonly synthesized in two steps (ref. 6). First, an aryl dianhydride is reacted with an aryl diamine in a polar solvent such as DMAc. This reaction yields a soluble polyamic acid (VII), which is often referred to as a prepolymer. In the second step, water is eliminated from the polyamic acid, by thermal or chemical means, to form the insoluble and infusible polyimide (VI).

The starting material in this synthesis of the chemically modified, or blocked, polyimide prepolymers was PMDA(I). The synthesis of the two isomeric polyimides is shown schematically in figures 1 and 2. PMDA was reacted with excess methanol to form the

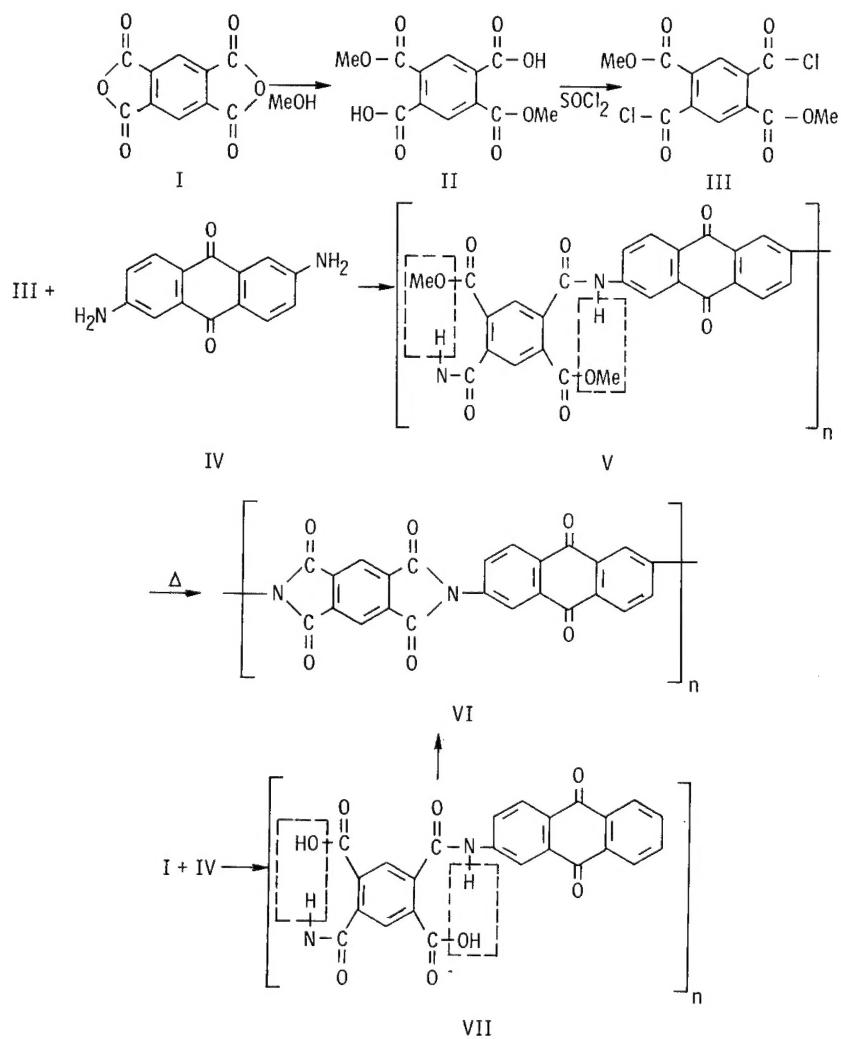


Figure 1. - Synthesis of polyimide from PMDA and 2,6-diaminoanthraquinone.

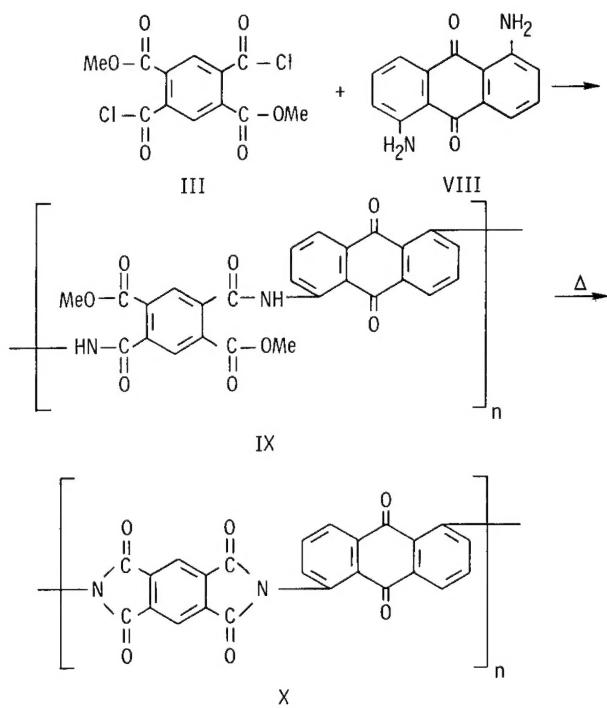


Figure 2. - Synthesis of polyimide from PMDA and 1,5-diaminoanthraquinone.

diester-diacid DMTA(II). Two structural isomers of II are possible as a result of the esterification reaction. The anhydride ring can be opened to form a product where the two carbomethoxy groups are para to each other (as shown in fig. 1). Alternately, the reaction can yield a product with the carbomethoxy groups meta to each other. In this study, only one product was isolated, identical to the para isomer described by Bell and Jewell (ref. 3).

The reaction of DMTA with thionyl chloride gave the diester-diacid chloride DMTC (III).

The blocked polyimide prepolymers were prepared by solution polymerization of equivalent amounts of DMTC and the diaminoanthraquinone at room temperature. The solvent used was DMAc, and the total solid content was kept at 5 to 10 percent.

Polymers from 2,6-DAQ. - The polymerization of DMTC and 2,6-DAQ went smoothly to yield the blocked prepolymer 2,6-DAQ BPP(V). The unblocked polyamic acid prepolymer 2,6-DAQ PAA(VII) was prepared in a similar manner by polymerization of PMDA and 2,6-DAQ in DMAc solution.

The polyimide 2,6-DAQ PI(VI) was obtained by thermal cyclization of either compound V or compound VII at  $300^{\circ}\text{C}$ . The formation of the polyimide from either prepolymer was monitored qualitatively by infrared spectroscopy. The polyimide samples from both 2,6-DAQ BPP and 2,6-DAQ PAA had identical infrared spectra (fig. 3(a)). On imid-

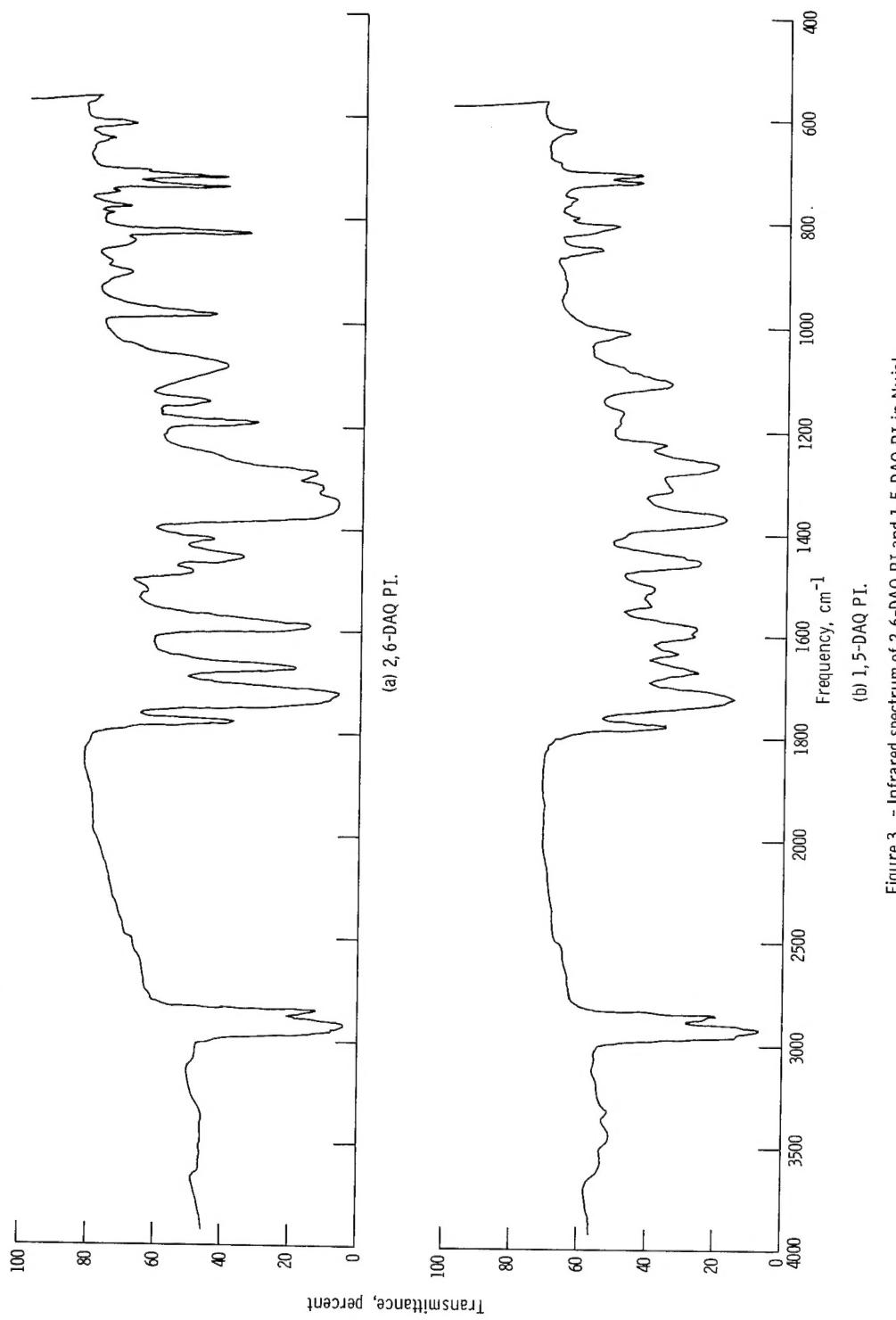


Figure 3. - Infrared spectrum of 2,6-DAQ PI and 1,5-DAQ PI in Nujol.

ization, the amide N-H stretch band of the prepolymers disappears, and the two imide carbonyl stretch bands of 2,6-DAQ PI appear at 1775 and 1720 centimeter<sup>-1</sup>.

The blocked prepolymer 2,6-DAQ BPP is more resistive to thermal ring closure than the unblocked polyamic acid 2,6-DAQ PAA. When the polyamic acid was heated in air at 200° C for 2 hours, it was completely converted to the polyimide. The blocked prepolymer, however, was only partially imidized under the same conditions.

Polymers from 1,5-DAQ. - Polymerization of DMTC and 1,5-DAQ gave the blocked prepolymer 1,5-DAQ BPP(IX), but the yield was low (about 10 percent), even after a prolonged reaction time (20 hr). The bulk of the product consisted of a low-molecular-weight oligomer mixed with unreacted starting materials. The inhibition of the polymerization reaction is probably caused by strong intramolecular hydrogen bonding between the amino hydrogen and the carbonyl oxygen of 1,5-DAQ.

The blocked prepolymer 1,5-DAQ BPP proved to be unusually stable toward thermal imidization. A sample, when heated at 200° C for 2 hours, showed a complete absence of imide carbonyl peaks in the infrared spectrum. The polyimide 1,5-DAQ PI(X) was obtained by heating the blocked prepolymer at 300° C for 2 hours. The infrared spectrum of 1,5-DAQ PI (fig. 3(b)) shows the typical imide carbonyl stretch bands at 1775 and 1720 centimeter<sup>-1</sup>.

It is interesting to note that attempts to prepare a polyamic acid prepolymer directly from PMDA and 1,5-DAQ were not successful. There was no evidence of a reaction at room temperature, even after 24 hours. When the reaction was carried out at the reflux temperature of DMAc, a soluble oligomer with a  $\bar{M}_w$  of about 1000 was obtained. The oligomer showed typical imide carbonyl stretch bands at 1775 and 1720 centimeter<sup>-1</sup>. The reaction presumably proceeded through an amic acid intermediate, which then was converted to the imide structure at the elevated reaction temperature.

### Solid-State Polymerization of 2,6-DAQ BPP

An important consideration in the manufacture of fiber-reinforced composites is the ultimate molecular weight of the polyimide. One can expect the thermomechanical properties of the composite to improve as the molecular weight is increased. One way to achieve a molecular weight increase is chain extension by means of solid-state polymerization of a polyimide prepolymer. After chain extension, the prepolymer should remain soluble and could then be advanced to the polyimide in the usual manner.

The solid-state polymerization reaction is favored by an increase of reaction temperature and time. However, increased temperature and time also promote cyclization of the prepolymer to the intractable polyimide structure. It has been found (ref. 1) that a polyamic acid prepared from PMDA and 4,4'-oxydianiline begins to cyclize to the poly-

imide before chain extension can occur. In contrast, chain extension of the corresponding diethylamide-blocked prepolymer was shown to be feasible (ref. 1).

In this study, solid-state polymerization of the blocked prepolymer 2,6-DAQ BPP was performed according to the technique of Hsu (ref. 7). When a sample of the prepolymer, with an initial  $\eta_{inh}$  of 0.263 deciliter per gram, was subjected to solid-state polymerization at 130° C for 48 hours, the  $\eta_{inh}$  was increased to 0.443 deciliter per gram. This corresponds to an increase of  $\bar{M}_w$  from 8500 to 16 800. The  $\bar{M}_w$  values should be regarded as only approximations, since they were calculated from the Mark-Houwink equation determined for a different prepolymer, namely, the polyamic acid from PMDA and 4,4'-oxydianiline (ref. 5). It is interesting to note that partial imidization of the product had occurred, but the sample was still completely soluble in DMAc. However, at temperatures above 130° C, the degree of imidization was sufficiently high to preclude full solubility of the product.

### Solvolytic Stability of 2,6-DAQ BPP

One of the problems in the manufacture of polyimide-fiber composites is the sensitivity of the polyamic acid prepolymer solutions to solvolytic degradation. It has been shown that the presence of water in DMAc solutions of polyamic acids causes a gradual decrease in viscosity (refs. 4 and 8). The viscosity decrease indicates a hydrolytic degradation of the polymer chain. Even when the polyamic acids were prepared in anhydrous DMAc, the solutions showed a viscosity decrease when kept at room temperature (refs. 4 and 8). The degradation was particularly severe for dilute solutions (approx 0.5 percent). This phenomenon raises the practical question of shelf life. It has been found that polyamic acid solutions can be stored for longer periods only at relatively high concentration (10 percent) and low temperature (-15° C). In addition, moisture must be strictly excluded (ref. 6). Previous studies have shown that solutions of a diethylamide-blocked polyimide prepolymer in anhydrous DMAc remain stable to solvolytic degradation. However, solutions of the same prepolymer in aqueous DMAc undergo a gradual hydrolysis, remaining stable for only 2 hours at room temperature (ref. 1).

In this study, solvolytic stability of the ester-blocked polyimide prepolymer 2,6-DAQ BPP was determined in both the presence and absence of water. A solution of 2,6-DAQ BPP in anhydrous DMAc at a concentration of 0.5 gram per deciliter showed no decrease in  $\eta_{inh}$  from its initial value of 0.430 deciliter per gram over a period of 510 hours. Likewise, a solution of 2,6-DAQ BPP in DMAc containing 1 percent water by volume showed no decrease in  $\eta_{inh}$  from an initial value of 0.435 deciliter per gram over the same time period. These results reveal that no solvolytic degradation occurred for the time period studied.

## Thermal Stability of Polyimides

One of the most important properties of a polymer considered for use as a high-temperature-resistant matrix material in fiber-reinforced composites is its thermal and thermo-oxidative stability. Some indication of this property can be obtained by the technique of thermogravimetric analysis (TGA), where the weight loss of the polymer is obtained during a constant rate of temperature increase.

The TGA curves indicating thermo-oxidative stability of the two isomeric polyimides in air are shown in figure 4. The polyimide 1, 5-DAQ PI exhibited about a 10 percent weight loss at  $490^{\circ}\text{C}$ . Rapid degradation of the polyimide began at  $500^{\circ}\text{C}$ , and it was degraded to 1 percent of its original weight at  $590^{\circ}\text{C}$ . In contrast, 2, 6-DAQ PI did not begin to lose appreciable weight until about  $575^{\circ}\text{C}$ , and was degraded to 1 percent of its weight at  $650^{\circ}\text{C}$ .

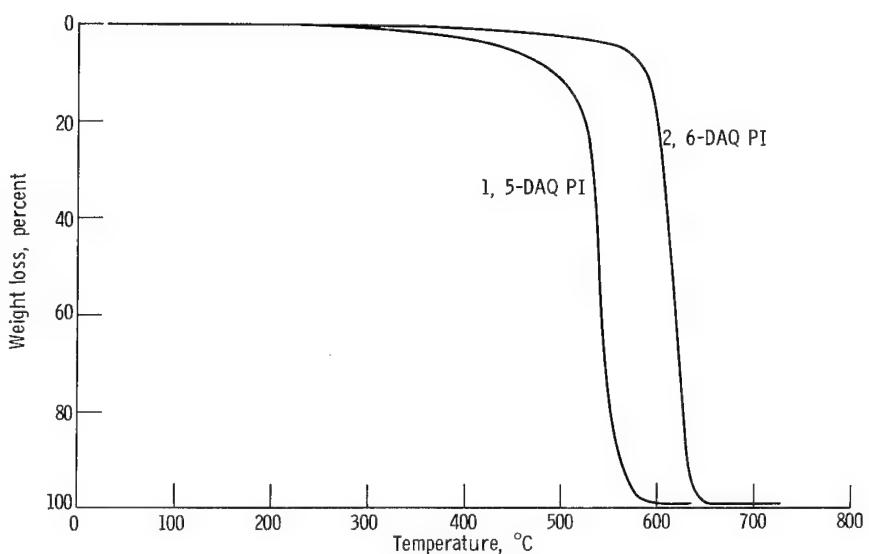


Figure 4. - Thermogravimetric analyses of polyimides. Atmosphere, air; heating rate,  $10^{\circ}\text{C}$  per minute; particle size, 60 to 80 mesh.

Figure 5 shows the TGA curves indicating the thermal stability of the two polyimides in nitrogen. 1, 5-DAQ PI began to degrade rapidly at about  $500^{\circ}\text{C}$  and had been reduced to 1 percent of its original weight at  $670^{\circ}\text{C}$ . The isomeric 2, 6-DAQ PI again showed greater stability, exhibiting only a 5-percent weight loss at  $560^{\circ}\text{C}$ . It then degraded rapidly during the temperature range of  $575^{\circ}$  to  $675^{\circ}\text{C}$ .

In isothermogravimetric analysis (ITGA) at elevated temperatures, a polymer is subjected more closely to the conditions it would experience under actual use in a fiber-reinforced composite. ITGA is therefore a better method for assessing thermal stability

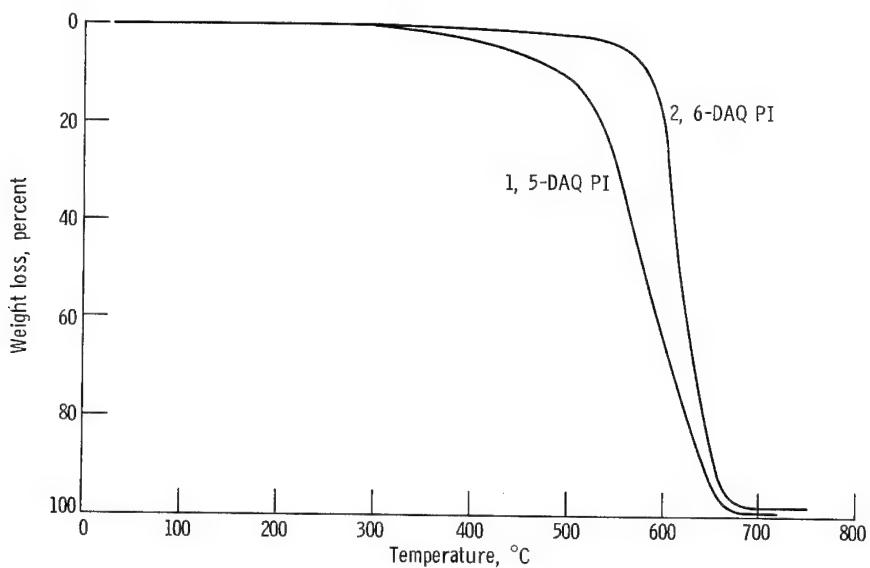


Figure 5. - Thermogravimetric analyses of polyimides. Atmosphere, nitrogen; heating rate  $10^{\circ}\text{C}$  per minute; particle size, 60 to 80 mesh.

than TGA. In ITGA, the weight loss of a polymer sample is measured as a function of time at a constant temperature. Figure 6 summarizes the results of isothermal aging of 2, 6-DAQ PI in dynamic air at various temperatures. At  $316^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ), the polyimide showed excellent thermal stability, having lost 12 percent of its original weight after 1000 hours. Since all ITGA runs were performed with powdered samples (particle size

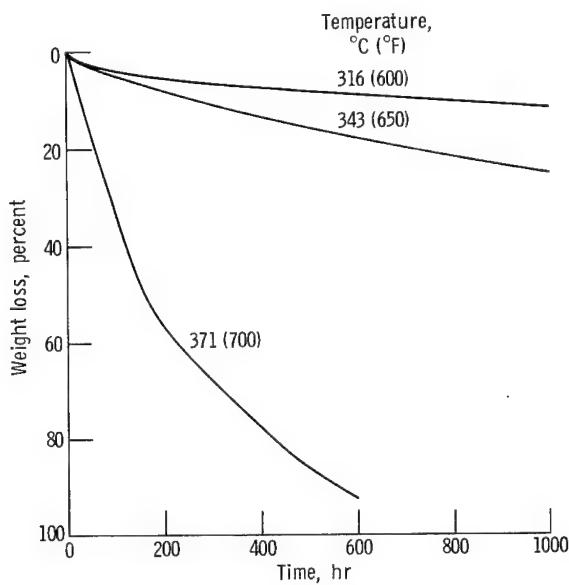


Figure 6. - Isothermogravimetric analysis of 2, 6-DAQ PI. Atmosphere, air; particle size, 60 to 80 mesh.

60 to 80 mesh) instead of molded specimens, the excellent weight retention is especially noteworthy. The polyimide still showed fair stability at 343° C (650° F). At this temperature, the sample had lost 25 percent of its weight after 1000 hours. For comparison, a commercially available polyimide sample (made from PMDA, but an unknown diamine) lost 26.9 percent of its weight under the same conditions. At 371° C (700° F), however, 2,6-DAQ PI degraded very rapidly. After 50 hours, the sample showed a 17-percent weight loss. The severe degradation continued with increased time, and the weight loss reached 92 percent after 600 hours.

### Miscellaneous Properties of 2,6-DAQ PI

Hydrolytic stability. - As expected, 2,6-DAQ PI displayed excellent hydrolytic stability in water. A powdered sample lost only 1.4 percent of its original weight after being boiled in a tenfold weight of water for 5 hours.

Solubility in acids. - As a rule, aromatic polyimides are soluble in mineral acids such as sulfuric acid or fuming nitric acid. The two polyimides prepared in this study, however, are nearly insoluble in these solvents. A powdered sample of 2,6-DAQ PI (250 mg) was shaken for 48 hours in 100 milliliters of fuming nitric acid at room temperature. After this treatment, the sample had lost only 6 percent of its orginal weight.

Reduction with sodium hydrosulfite. - Aromatic polyimides are insoluble in organic solvents. Therefore, in the preparation of fiber-reinforced composites, the polymer must be used as a prepreg resin while it is still in the soluble prepolymer stage. It was anticipated that, similar to anthraquinone vat dyes, soluble polyimides might be prepared by reduction of the quinone function to the soluble hydroquinone with sodium hydrosulfite in an alkaline medium. Then, on exposure to acid conditions and air, the hydroquinone would be reoxidized to the original insoluble quinone structure. The 2,6-DAQ PI could indeed be dissolved by treatment with sodium hydrosulfite in boiling aqueous sodium hydroxide. The polymer precipitated out of solution on acidification. However, the infrared spectrum of the product showed complete hydrolysis to the polyamic acid. Even when the hydrosulfite reduction was carried out at room temperature, partial hydrolysis to the polyamic acid had occurred. This method for solubilizing the polyimide is, therefore, not practical because of the extensive hydrolysis to the polyamic acid.

### CONCLUDING REMARKS

Two new polyimides with a high thermal stability were synthesized from pyromellitic dianhydride and two isomeric diaminoanthraquinones. The diamines used were 1,5-

diaminoanthraquinone (1, 5-DAQ) and its 2, 6-isomer (2, 6-DAQ). The synthesis was achieved through chemically modified, or blocked, prepolymer intermediates, using methanol as the blocking reagent. The weight-average molecular weight  $\bar{M}_w$  of the blocked prepolymer from 2, 6-DAQ was increased by the technique of solid-state polymerization. When the reaction was carried out for 48 hours at  $130^{\circ}\text{C}$ , the  $\bar{M}_w$  was nearly doubled, from 8500 to 16 800. The blocked prepolymer from 2, 6-DAQ showed excellent solvolytic stability. Its solution in N,N-dimethylacetamide containing 1 percent water showed no decrease in inherent viscosity for 510 hours from an initial value of 0.435 deciliter per gram. The blocked prepolymer from 2, 6-DAQ was more resistant to thermal imidization than the corresponding polyamic acid. While the polyamic acid underwent complete imidization after heating in air at  $200^{\circ}\text{C}$  for 2 hours, the blocked prepolymer from 2, 6-DAQ was only partially imidized under the same conditions. The blocked prepolymer from 1, 5-DAQ was even more resistant to thermal imidization; under the aforementioned conditions, no imidization had occurred.

The polyimides from the two isomeric diaminoanthraquinones exhibited excellent thermal stability. Thermogravimetric analysis showed that the polyimide from 1, 5-DAQ was stable to temperatures in excess of  $500^{\circ}\text{C}$  in both air and nitrogen. The isomeric polyimide from 2, 6-DAQ exhibited thermal stability in excess of  $550^{\circ}\text{C}$  under the same conditions. The polyimide from 2, 6-DAQ also showed remarkable thermal stability when subjected to isothermogravimetric analysis. A powdered sample (60 to 80 mesh) of the polyimide retained 88 percent of its weight after heating in air at  $316^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) for 1000 hours. The weight retention was 75 percent when aging was carried out at  $343^{\circ}\text{C}$  ( $650^{\circ}\text{F}$ ).

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, March 9, 1970,  
129-03.

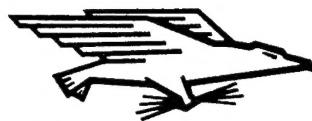
## REFERENCES

1. Delvigs, Peter; Hsu, Li-Chen; and Serafini, Tito T.: The Synthesis of a Novel Polyimide Precursor. NASA TN D-5184, 1969.
2. Marvel, Carl S.: Synthesis of Thermally Stable Polymers. Arizona Univ. (AFML-TDR-64-39, pt. 6, DDC No. AD-850027), Mar. 1969.
3. Bell, V. L.; and Jewell, R. A. Synthesis and Properties of Polyimidazopyrrolones. J. Polymer Sci.-Polymer Chem., pt. A-1, vol. 5, no. 12, Dec. 1967, pp. 3043-3060.

4. Sroog, C. E.; et al.: Aromatic Polypyromellitimides from Aromatic Polyamic Acids. *J. Polymer Sci.-General Papers*, pt. A, vol. 3, no. 4, Apr. 1965, pp. 1373-1390.
5. Wallach, M. L.: Aromatic Poly(amic Acids): Fundamental Structural Studies. *J. Polymer Sci.-Polymer Phys.*, pt. A-2, vol. 5, no. 4, July 1967, pp. 653-662.
6. Sroog, C. E.: Polyimides. *J. Polymer Sci.-Polymer Symposia*, pt. C, no. 16, 1967, pp. 1191-1209.
7. Hsu, Li-Chen: Synthesis of Ultrahigh Molecular Weight Poly(ethylene terephthalate). *J. Macromol. Sci.-Phys.*, vol. B1, no. 4, Dec. 1967, pp. 801-813.
8. Bower, G. M.; and Frost, L. W.: Aromatic Polyimides. *J. Polymer Sci. - General Papers*, pt. A, vol. 1, no. 10, Oct. 1963, pp. 3135-3150.

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